Reaction of a Bituminous Coal with the Potassium-Crown Ether Reagent

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Introduction

It is generally accepted that a bituminous coal is best represented as a macromolecular, highly cross-linked, three-dimensional structure with aromatic clusters cross-linked by ether and alkane bridges and hydrogen bonds (1,2). Therefore, most coal conversion reactions involve reacting coal under severe conditions of temperature and pressure. As a result of the severe conditions, bond cleavage was nonselective and often accompanied by retrogressive (bond-forming) reactions. In this paper, we report on the reaction of a bituminous coal with a powerful yet selective site-specific reagent, namely, potassium-crown ether operating at *room temperature* and *atmospheric pressure*. The potassium-crown ether reagent can generate a stable solution of electrons at room temperature and atmospheric pressure (3,4). The small size of the electron and its high reactivity permits it to diffuse into the macromolecular coal network and transfer onto the aromatic substrates in the coal. This results in the formation of aromatic radical anions or dianions which undergo cleavage reactions at ether (5,6) and diaryl alkane linkages (7,8). Furthermore, crown ethers act as phase transfer catalysts in promoting the electron transfer to the solid coal. The reduction of the aromatic rings to dihydro or tetrahydro products occurs along with the cleavage reactions (9).

Experimental

A 250 ml round bottom flask was flame dried and flushed with nitrogen. Potassium metal (2.96 g, 75 mmole) was cleaned and cut under hexane and transferred into the round bottom flask in a nitrogen atmosphere glove box. The flask was again flame dried and flushed with nitrogen to remove traces of hexane. 100 ml THF solution of crown ether (4.0 g, 15 mmole) was added to the potassium metal via a double-ended needle. A dark blue solution was obtained which was cooled to $0^{o}C$ in an ice bath for 30 minutes. One gram of Illinois No. 6 coal (C=74.69%; H=5.44%; N=1.88%;O=18.06%; 100 mesh) was added to the K-CE/THF solution using a transferring tube which was originally attached to the round bottom flask. The reaction mixture was stirred for 48 hours under nitrogen at room temperature. It was then cooled to $0^{o}C$ and quenched with water. The THF was removed by rotaevaporation. The aqueous slurry of the coal was freeze-dried to remove the water. The work-up of the reacted coal is shown in Figure 1.

Results and Discussion

The Illinois No. 6 bituminous coal was reacted with the potassium-crown ether reagent at room temperature and atmospheric pressure. The reaction mixture was quenched with water and fractionated into THF extracts and alkali-solubles as shown in Figure 1. For each K-CE reaction, 15-20% of the coal was solubilized into THF and aqueous alkali fractions. After the third and fourth K-CE reactions, about 50% and 75% of the original coal was

solubilized, respectively. The formation of the alkali-soluble coal fragments indicated that ether linkages are being cleaved to form phenolic coal fragments.

Table 1. Total Solubility of Illinois No. 6 Coal
inr Each Fraction After Three and Four K-CE Reactions

Notebook #	THF-1 (%)	ALK (%)	THF-2 (%)	Total Solubility	
				Solubles	Residue
H2-52A (A-C) Three K-CE Reactions	9.9	26.9	14.7	51.5	51.2
H3-6 Four K-CE Reactions	13.7	51.6	12.8	78.0	22.8

The reason for successive K-CE reactions is due to certain limiting steps in the electron transfer process: (1) concentration of the solvated electrons in solution-more concentration of electrons, greater would be the transfer to the aromatic substrates in coal which in turn would mean greater cleavage and reduction reactions being initiated; (2) intrinsic repulsive barrier of the negatively charged aromatic substrates generally by the initial electron transfer; and (3) mass transport limitations. Obviously, one can increase the solubility of the coal into the various fractions by optimizing the potassium-crown ether to coal ratio, reaction time, temperature, and etc. However, successive potassium-crown ether reaction allows us to selectively snip at the macromolecular network at room temperature and atmospheric pressure conditions to prepare solubilized coal fragments with are amenable to detailed chemical, spectroscopic, chromatographic, and mass spectrometry analysis.

The elemental composition of each soluble fraction (THF-1, alkali, THF-2) and insoluble coal residue was determined by microanalysis. (Table 2). The hydrogen to carbon ratios are also included in Table 2. The results showed that after each K-CE reaction of coal there is an increase in the number of hydrogen atoms. The overall hydrogen uptakes are 7, 18, and 22 per 100 C-atoms for first, second, and third K-CE treatment, respectively. The hydrogen uptake is due to reactions such as Birch-Huckel-type reduction, cleavage of aliphatic bridges and ether linkages occurring during the K-CE reaction with coal.

Both THF extracts (THF-1 and THF-2) have higher H/C ratio as compared to the alkali soluble fraction and the insoluble residue during each K-CE reaction. A gradual increase in H/C ratio for each fraction after second and third consecutive K-CE treatment was also observed. This result corresponds well with the overall increase in hydrogen content and suggests further that reduction and cleavage of coal molecules upon additional K-CE treatment were occurring.

Figure 2 shows the infrared spectra of the various extracts obtained from the K-CE reaction with the coal. The IR spectrum of THF-1 extract was dominated by sharp aliphatic CH stretching bands just below 3000 cm^{-1} suggesting that this extract contains predominantly aliphatic material. This finding is in agreement with the high H/C ratio obtained for this extract. The spectrum of THF-2 extract also showed the dominating C-H stretching vibrations just below 3000 cm^{-1}; however, a broad OH stretching vibration in the

Table 2. Elemental Analysis of K-CE Treated Coal

| | Analysis (wt%) (daf) | | | | H/C |
	C	H	N	O	
Illinois No. 6 untreated coal	74.69	5.44	1.88	18.06	0.87
(1st K-CE Reaction)					
2-52A-THF-1	79.00	8.74	2.35	9.90	1.33
2-52A-Alk	71.76	5.90	1.55	20.77	0.99
2-52A-THF-2	74.02	7.04	0.81	18.14	1.14
2-52A-Res	73.23	5.95	1.28	19.50	0.90
(2nd K-CE Reaction)					
2-52A-THF-1	75.01	7.96	0.44	16.59	1.28
2-52A-Alk	68.34	5.97	0.90	24.80	1.05
2-52A-THF-2	67.93	7.22	0.56	24.20	1.28
2-52A-Res	74.12	6.27	0.71	19.70	1.02
(3rd K-CE Reaction)					
2-52A-THF-1	-	-	-	-	-
2-52A-Alk	71.00	6.67	0.99	21.34	1.13
2-52A-THF-2	70.67	7.51	0.77	21.05	1.28
2-52A-Res	73.00	6.54	1.02	1.94	1.08

Note: THF-1: THF extract of alkali residue
 Alk: Aqueous alkali soluble fraction after THF-1 extraction
 THF-2: THF extract of acidified residue after THF-1 and Alkali
 extraction

3400-3200 cm^{-1} was also present. Thus, the THF-2 extract also contains aliphatic material which may be attached to a hydroxy aromatic ring system. Again, the increased H/C ratio nicely corroborates the presence of aliphatics. Both THF extracts showed carbonyl absorptions around 1710 cm^{-1}. The alkali-soluble fraction showed a strong carbonyl stretching vibration at 1700 cm^{-1} coupled with a broad O-H stretching vibration extending down from 3500 cm^{-1}. The infrared spectrum of the residue was similar to the untreated coal but showed weak carbonyl absorption bands.

The carbonyl absorption bands present in the IR spectra of all the extracts suggests that reduction of phenolic units to cyclohexanone (i.e., OH to C=O) units was a major reaction pathway in the reaction of coal with the K-CE reagent. The reduction of phenols and naphthols to the corresponding dihydro or tetrahydro aromatic carbonyl compounds by the K-CE reagent has been confirmed by us using model compounds. More work needs to be done to clarify the reaction mechanism; however, the increased hydrogen content of the alkali soluble and residue fractions on consecutive K-CE treatments of coal supports this reduction chemistry. The reasons for the carbonyl components to be fractionated into an alkali soluble fraction, an insoluble residue fraction, and in the THF extracts are: (1) carbonyl units that can undergo a keto-enol-tautomerism would be rendered alkali soluble; (2) the cyclohexanone type units which are hooked to coal phenolic units would also be alkali soluble; and (3) the carbonyl components in the THF extracts would be the relatively nonpolar components.

Figure 3 shows the proton NMR spectrum of the THF-1 extract. The spectrum confirmed the presence of predominantly aliphatic material in this extract. Thus, the dominant sharp signal at 1.2 ppm is characteristic for methylene protons of long-chain polymethylenes. The group of signals in the 2-3 ppm region can be assigned to dihydro aromatic protons. Based on the mechanism of the K-CE reaction reduction of the aromatic ring to dihydro and even tetrahydro aromatics was expected and the NMR evidence nicely corroborates it. Thus, one of the major constituents of this extract is long-chain polymethylenes which may or may not be attached to a hydroaromatic ring system. The ^{13}C NMR spectrum (Figure 4) also strongly supported the presence of long-chain polymethyelene groups in the extract. The most intense signal is at 30.2 ppm which is generally assigned to the internal methylene carbons of straight-chain alkanes (an average carbon chain length of approximately 8). The presence of a broad spectral envelope in the 15-50 ppm region in addition to the sharp alkane lines is indicative of the extract's complexity arising out of the presence of only small amounts of these polymethylene-type compounds. The broad complex band of carbon signals in the 120-130 ppm region is due to the aromatic and polycyclic aromatic species of the extract.

Detailed characterization of the polymethylenes in the THF-1 extract was done using chemical ionization mass spectrometry and tandem mass spectrometry (MS/MS) (10,11). Tandem mass spectrometry is a well-established technique for the direct analysis of complex mixtures, because it can do unaided separation and identification of the constituents of the mixtures. By using different scan types, the structure of individual components can be identified and the presence of series of related compounds can be ascertained. In particular, daughter scans identify specific constituents of the mixture on the basis of molecular weight and fragmentation behavior.

Figure 5 shows the CI mass spectrum of the THF-1 extract. In it, one can identify 14 sets of three intense peaks; each set separated by 14 amu. Based on the molecular weight, the first set of three peaks at m/z 129, 131, and 133 can be assigned to the protonated molecular ions of naphthalene, dihydronaphthalene, and tetralin. It follows that the remainder sets of three intense peaks represented the homologous series of alkylnapthalenes, alkyldihydronaphthalenes, and alkyltetralins, with the polymethylene chain extending up to 14 carbons (Figure 6). In all probability, the dihydronaphthalene series and the tetralin series arise by *Birch Reduction* of the naphthalene compounds during the K-CE reaction. Therefore, only the homologous series of alkyl naphthalene compounds may be present in the coal. There are other molecular ions present but their intensities are well below that of the naphthalene-polymethylene series.

It was indeed surprising to obtain such a clean CI mass spectrum in which the polymethylene molecular ions predominate. Normally, mass spectra of coal mixtures is complex and messy and no clear-cut compound series can be identified. The reason we obtained such a clean spectrum is because the analysis was done on the THF-1 extract obtained from the second K-CE reaction. In the first K-CE reaction all the extractable material in coal and other compounds associated with coal will be removed during the THF extraction, alkali extraction and another THF extraction steps, leaving behind a *pristine* coal macromolecule. This strongly implies that the polymethylenes are not present as "trapped molecules" but as an integral part of the coal macromolecular matrix. The polymethylene chain could be present as crosslinks between aromatic clusters or as long dangling side chains on an aromatic ring.

Daughter spectra (Electron Impact) were taken for each and every member of the homologous series to confirm the structural identity of the polymethylene compounds.

Summary

The reaction of a bituminous coal with the K-CE reagent resulted in the selective sniping of the linkages in the coal macromolecular network at *room temperature* and *atmospheric pressure*. Soluble chunks of coal fragments were obtained without recourse to any thermal or pressure effects. In addition to ether cleavage reactions, a major reaction pathway in the coal/K-CE reaction is the reduction of phenolic groups to carbonyls. Analysis of the THF-1 extracts revealed the presence of a homologous series of alkyl naphthalenes and alkyl tetralins, with the methylene chain extending up to 14 carbon atoms, as the major components in the extract. These compounds are *real* and an integral part of the coal matrix and not present as *trapped molecules*. Any representation of *coal structure* or the development of *coal process models* would have to account for these pockets of *aliphatic rich zones*.

Acknowledgments

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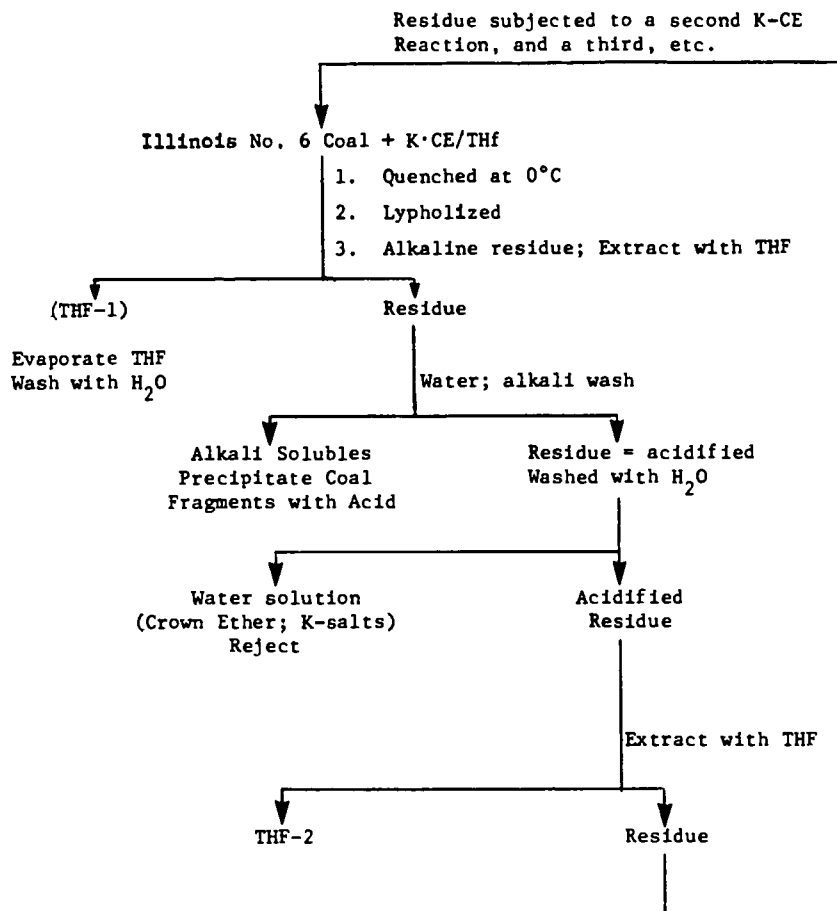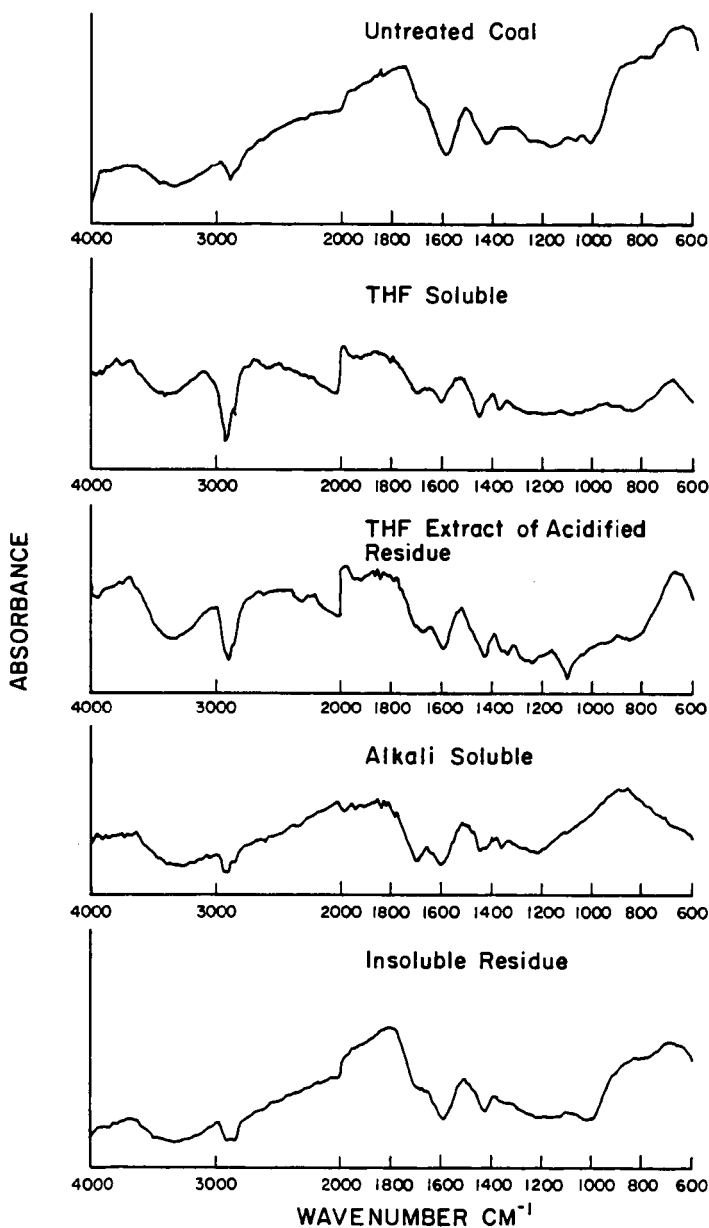
Residue subjected to a second K-CE
Reaction, and a third, etc.

Illinois No. 6 Coal + K·CE/THf

1. Quenched at 0°C

2. Lypholized

3. Alkaline residue; Extract with THF

(THF-1)   Residue

Evaporate THF
Wash with H_2O Water; alkali wash

Alkali Solubles   Residue = acidified
Precipitate Coal   Washed with H_2O
Fragments with Acid

Water solution   Acidified
(Crown Ether; K-salts)   Residue
Reject

Extract with THF

THF-2   Residue

Figure 1.   Work-Up of the Coal/K-CE Reaction.

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ABSORBANCE

Untreated Coal

4000   3000   2000 1800 1600 1400 1200 1000 800 600

THF Soluble

4000   3000   2000 1800 1600 1400 1200 1000 800 600

THF Extract of Acidified
Residue

4000   3000   2000 1800 1600 1400 1200 1000 800 600

Alkali Soluble

4000   3000   2000 1800 1600 1400 1200 1000 800 600

Insoluble Residue

4000   3000   2000 1800 1600 1400 1200 1000 800 600

WAVENUMBER CM^{-1}

Figure 2.   Infrared spectra of different fractions of K-CE treated
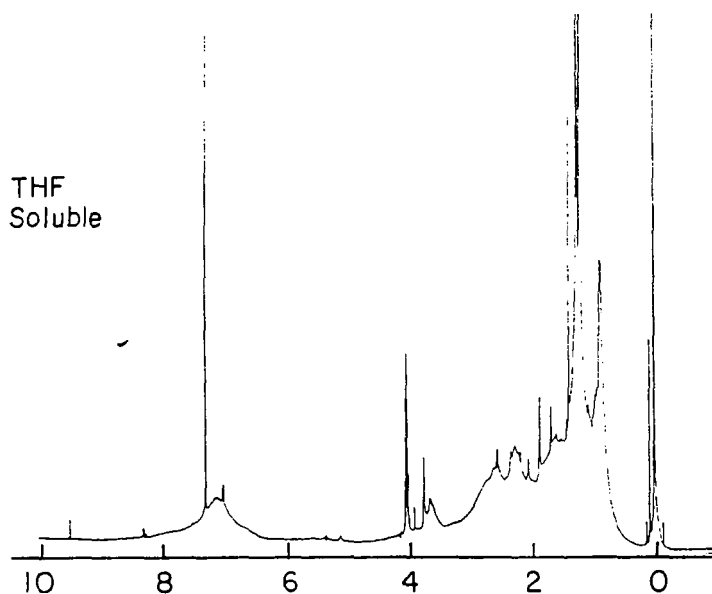Illinois No. 6 Bituminous Coal.

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THF
Soluble
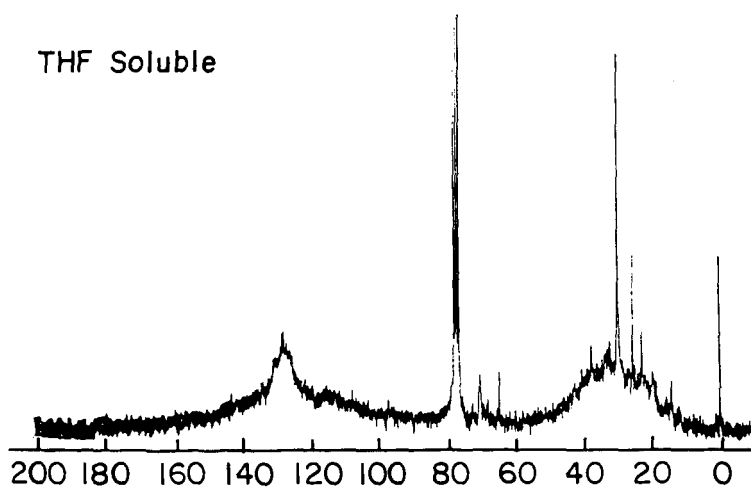

Figure 3. ^{1}H NMR of THF-1 extract.

THF Soluble

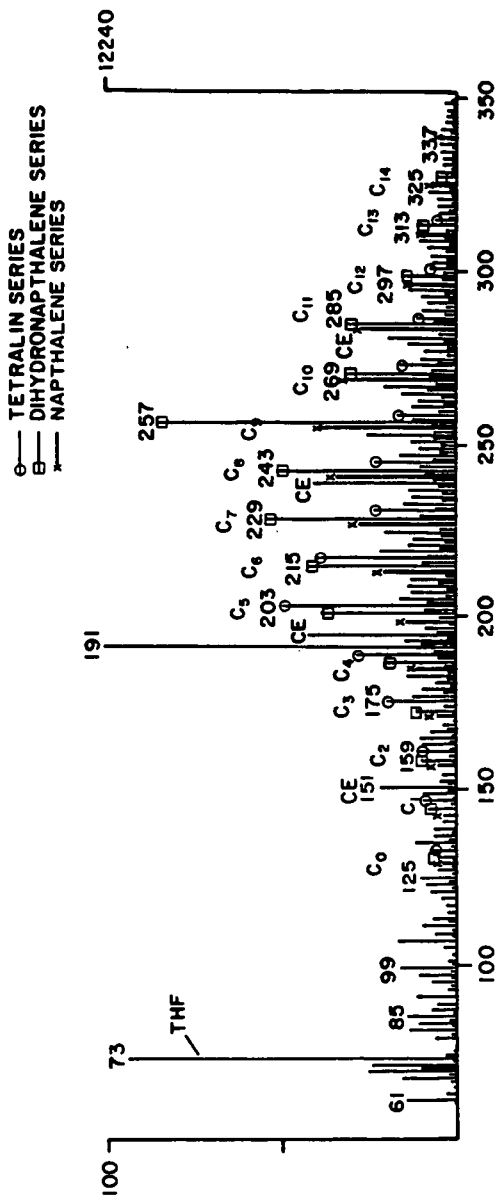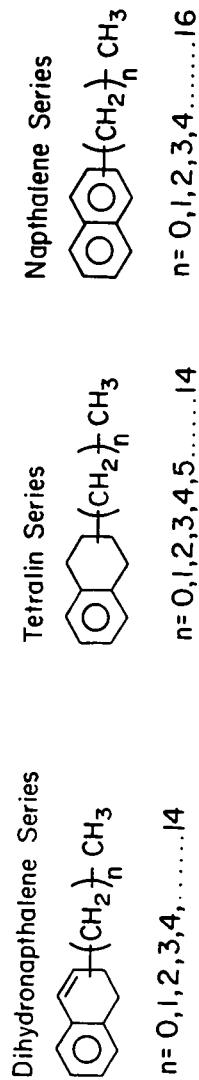Figure 4. ^{13}C NMR of THF-1 extract.

Figure 5. Chemical ionization mass spectrum.

Figure 6. Polymethylene structures in coal.

Dihydronapthalene Series

$n = 0,1,2,3,4,\ldots\ldots14$

Tetralin Series

$n = 0,1,2,3,4,5,\ldots\ldots14$

Napthalene Series

$n = 0,1,2,3,4,\ldots\ldots16$

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